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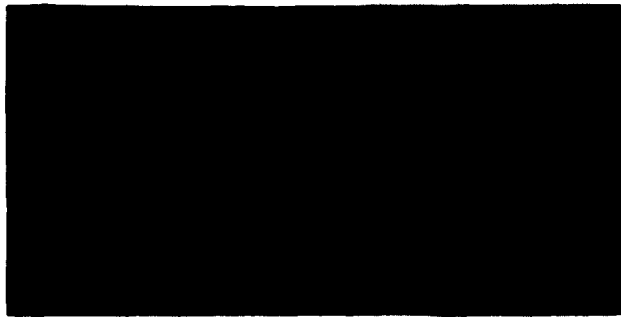
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BASIC STUDIES ON FUEL CELL SYSTEMS

. February 1962

Prepared Under Navy, Bureau of Weapons

Contract NOw 60-0738-d

Quarterly Report No. III

3 November 1961 Through 12 February 1962

LOCKHEED MISSILES & SPACE COMPANY
A Group Division of Lockheed Aircraft Corporation

3591

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A Group Division of Lockheed Aircraft Corporation
Sunnyvale, California

FOREWORD

The work described in this quarterly report was conducted
in the Electrochemistry Research Department, under the
overall direction of Dr. George B. Adams. Dr. Theodore
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ABSTRACT

The alkaline, aqueous hydrazine, ammonia and formaldehyde anodes, and the intermediate ammonia-oxygen fuel cell system were evaluated. Preliminary results were obtained with alkaline oxygen and air cathodes.

The most feasible systems were found to be the aqueous hydrazine and the aqueous ammonia oxygen or air fuel cells.

The acid electrolyte studies of the aforementioned systems will be continued, and fundamental studies involving the theory and optimization of fuel cell design, construction, and operation will begin.

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SUMMARY

The following work on the investigation of the kinetics of electrode reactions in alkaline systems has been accomplished:

- Evidence that hydrazine is anodically oxidized through hydrogen as an intermediate in alkaline electrolyte was obtained.
- Reduction of the surface area of the hydrazine black platinum anode catalyst was investigated for possible optimization with respect to hydrazine decomposition rate and anode polarization.
- Hydrazine anode gases were analyzed at closed and open circuits.
- Hydrazine was shown to be consumed at the cathode in multiple-cell fuel cells.
- The molten caustic ammonia anode was shown to oxidize ammonia to nitrate and nitrite at 150°C.
- The black platinum formaldehyde anode was found to have poor life in alkaline electrolyte, and the work suggests that self-poisoning occurs.

The electrochemical characteristics of the alkaline, aqueous hydrazine, ammonia and formaldehyde anodes were studied, and the molten caustic ammonia-oxygen fuel cell was studied from the standpoint of life and nitrate-nitrite formation.

The oxygen and air oxidants were compared, using both carbon and metal cathodes in alkaline solution. Some energy calculations were made for a number of practical fuel cell systems.

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ILLUSTRATIONS

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TABLES

NOMENCLATURE

$E°$	standard potential (Ref. 1)
E_a	anode potential (as measured against a reference electrode)
E_c	cathode potential
E_{ao}, E_{co}	open-circuit anode, cathode potential
V_c	cell potential
V_o	open-circuit cell potential
ΔE_a, ΔE_c	anode, cathode polarization
I	current density
i	current
ΔP_c	pressure drop across cathode
R	electrical resistance
Hg-HgO	a Hg-HgO, 6.90 M KOH reference cell

Section 1

INTRODUCTION

It is generally agreed that system optimization of electrochemical fuel cells is of significant value after definite knowledge of the specific components is available. After the electrodes and electrolyte have been studied, both alone and in relation to each other, the resultant operational requirements and performance of the components can be applied to design a complete package unit.

In this connection, basic research has been done on the following:

- Hydrazine anode
- Formaldehyde anode
- Aqueous ammonia anode
- Molten caustic ammonia anode
- Oxygen and air cathodes

Alkaline electrolyte systems have been used throughout this work, and study of acid electrolytes will begin next quarter. A completely developed fuel cell system would conceivably be some combination of the component anodes and cathodes listed above.

The use of aqueous hydrazine, formaldehyde, and ammonia fuels at ambient temperatures and pressures has been considered. Operation at ambient temperatures, of course, obviates the necessity of an initial warmup period, although temperatures slightly higher than ambient temperatures would be attained in practice because of the internal resistance of the cell. Intermediate-temperature molten caustic ammonia fuel cells have the advantage of facilitating water product removal by evaporation.

Basic research on the anode and cathode systems listed is continuing, and, concurrently, some preliminary engineering development of batteries employing 4-in.

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electrodes in hydrazine-oxygen systems is being completed. Power output with this system was found to be great enough to warrant the immediate developmental investigation. This work was particularly fruitful because it indicated the feasibility of a hydrazine-oxygen or hydrazine-air system in fuel cell operation. It also resulted in the findings that hydrazine fuel is lost at the cathode and that pressed carbon cathode life is reduced by this interaction. The extent of hydrazine loss was determined, and its importance was evaluated.

Some initial estimates of the weights and power output of small hydrazine-oxygen fuel cell batteries were made. In addition, some estimates were made of the energy-to-weight ratio of various fuels which were used with oxygen and air. The latter are necessarily theoretical and do not yield the results ultimately attainable through an intensive development program.

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Section 2

EXPERIMENTAL WORK

2.1 HYDRAZINE ANODE IN ALKALINE SOLUTION

2.1.1 Electrochemical Characteristics

Experimental apparatus. The apparatus used in this work was of the type previously
described in the investigation of aqueous ammonia anodes (Ref. 2). Figure 1 shows
the components of the test cell used for measuring the anode potential and current
density. The anode is a black platinum, electroplated, porous nickel electrode which
has been sintered in hydrogen atmosphere at 300°C and cooled in argon. (Preparation
of the anode is described in detail in Appendix A.) The anode presents approximately
5 cm^2 of apparent surface to the electrolyte, which is pumped through the anode from
a reservoir at the rate of 1 cm/sec. The volume of electrolyte is usually 2 liters, and
the electrolytic concentration remains essentially constant during a measurement or
series of measurements. The cathode and anode chambers are separated by a cello-
phane membrane, and the catholyte is not circulated.

The anode block, housing the anode to be tested, is shown in Fig. 2. Electrical con-
tact with the anode is by means of a screen which is pressed to the anode. This screen
contains a sheet-metal tab which leads to the outside through two neoprene gaskets for
external electrical connections. In some experiments, the tab was welded directly to
the anode. For the coulombic efficiency runs, a combination gas eudiometer and gas-
liquid separator (Fig. 3) was placed in the outlet electrolyte line.

Open-circuit potential. In Table 1 are listed the open-circuit potentials measured for
the polarization and coulombic efficiency runs for three typical anodes in 0.2 M hydra-
zine, 30-percent KOH, at 26°C. The average value was found to be 0.906 v versus a

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BOLTING ARRANGEMENT

END PLATE

H_2 GAS OUT

ELECTROLYTE OUT

SEE DETAIL DRAWING

ELECTROLYTE IN

E

D

C

B

A

TO REFERENCE CELL

UNITS NOT SHOWN:

A GASKET
B GASKET, ANODE, TAB, GASKET
C GASKET, TAB, ANODE, GASKET
D GASKET, MEMBRANE, GASKET
E GASKET, CATHODE, GASKET

TO REFERENCE CAPILLARY

MERCURY

MERCURIC OXIDE

REFERENCE CELL
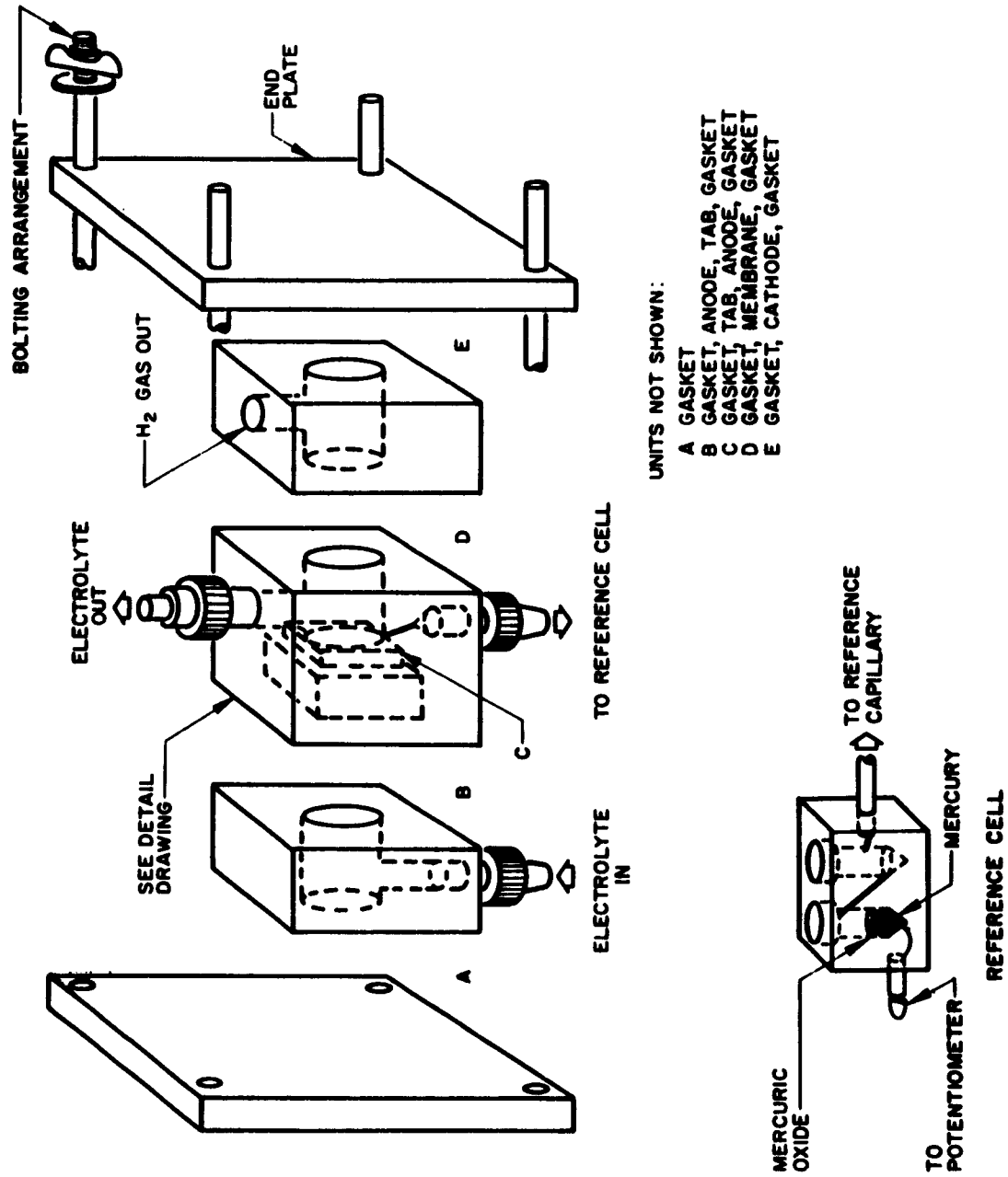
TO POTENTIOMETER

Fig. 1 Testing Cell Assembly

PLEXIGLASS COMPONENTS

STAINLESS-STEEL
FASTENING BOLTS

HOLDING
BLOCK

ELECTROLYTE
FLOW

ANODE

REFERENCE
CAPILLARY

ANODE
BLOCK

TO BRIDGE
AND
REFERENCE CELL
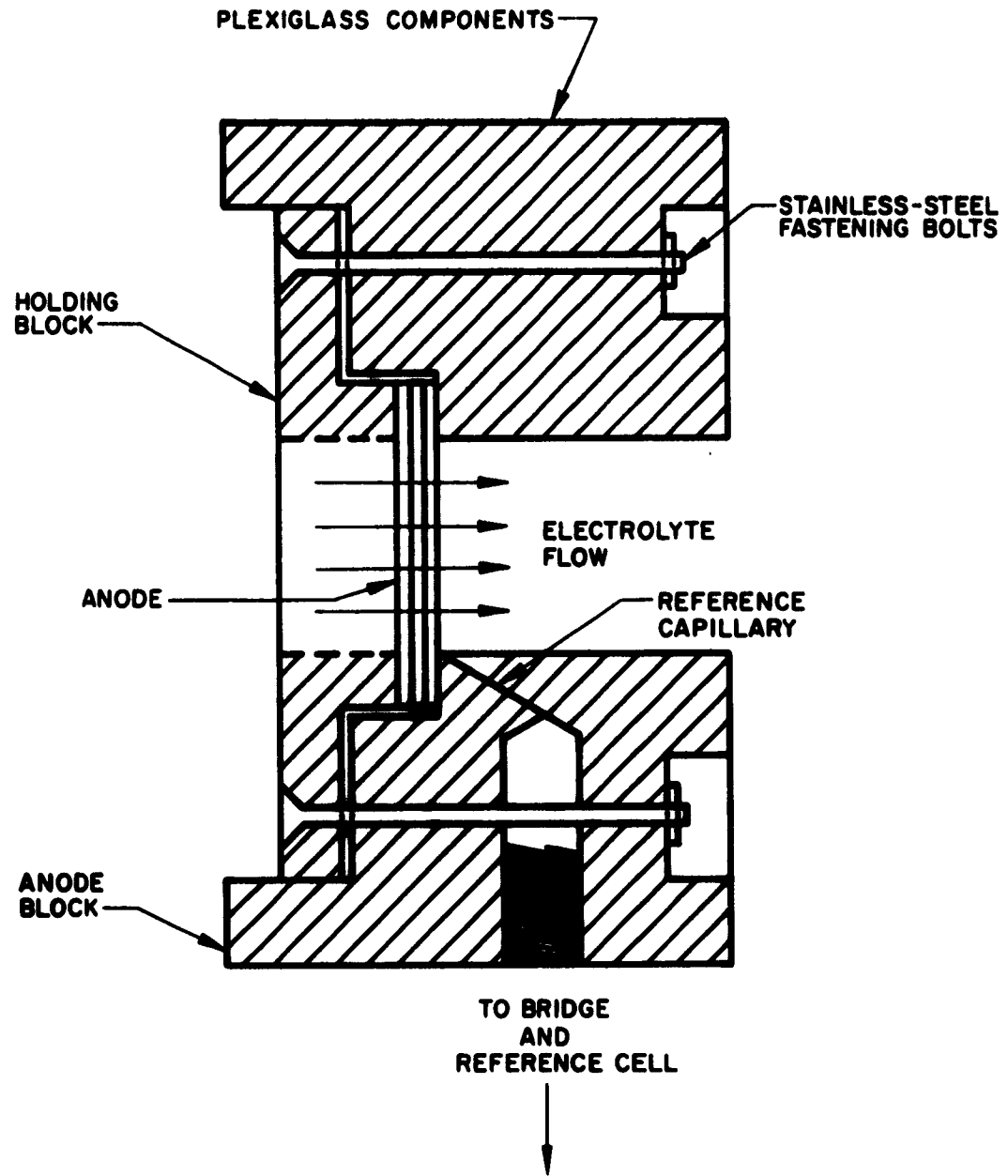
Fig. 2 Detail of Anode Block

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TO GAS SAMPLE BULB

PURGING TUBE

EUDIOMETER
MEASURING TUBE

LEVELING
BULB

OUTLET TUBE
FOR THERMOSTAT LIQUID

GAS
SEPARATION

GAS-FREE ELECTROLYTE
FLOW TO RESERVOIR

ELECTROLYTE-GAS
MIXTURE FROM
TEST CELL ASSEMBLY
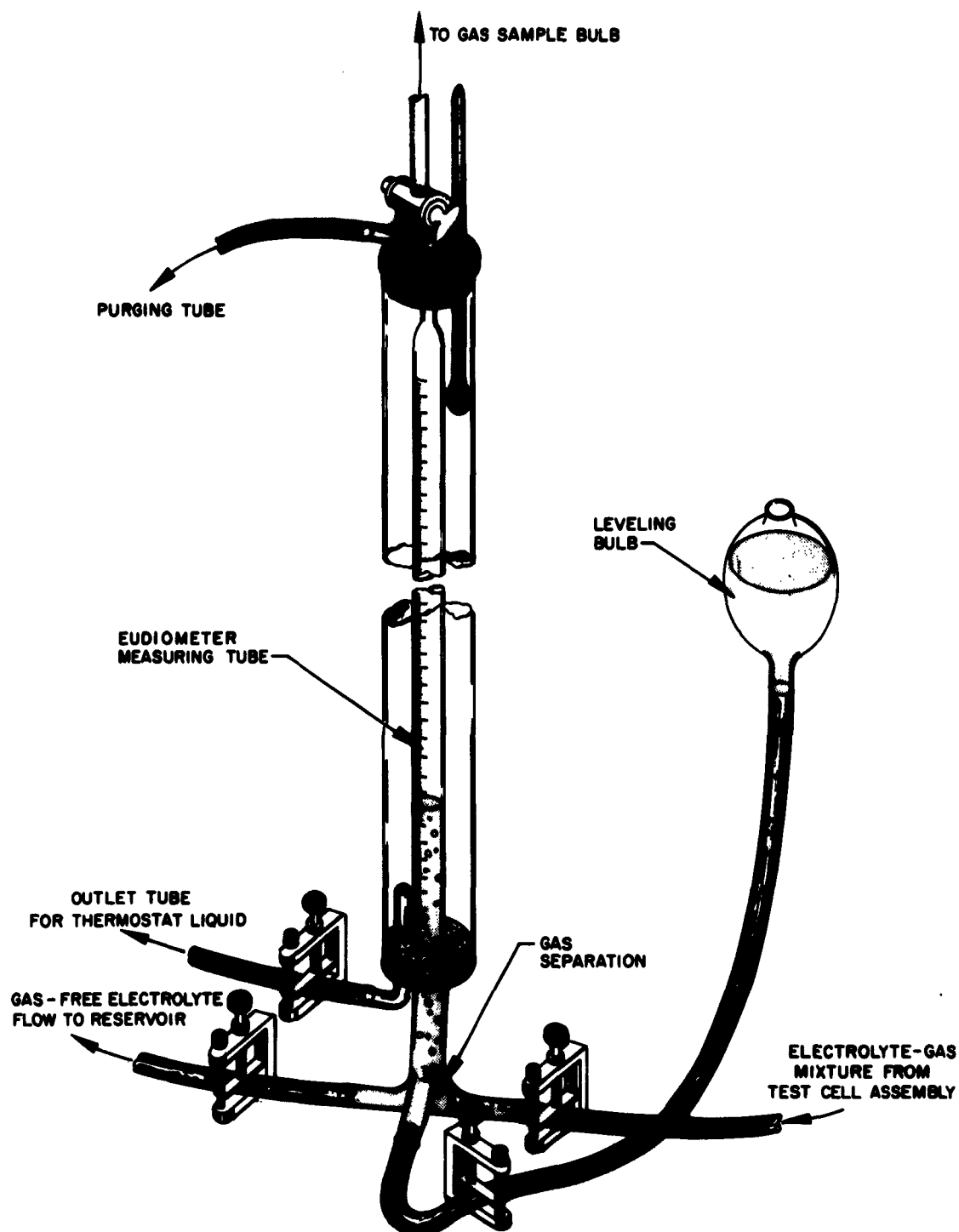
Fig. 3 Gas-Liquid Separator and Eudiometer Assembly

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Table 1

OPEN-CIRCUIT POTENTIALS OF BLACK PLATINUM, POROUS NICKEL
ANODES IN 0.2 M HYDRAZINE, 6.90 M KOH, AT 26°C,
HEAT TREATED AT 300°C

Anode No.	Volts Vs. a Hg-HgO Ref.	Volts Vs. a Standard Hydrogen Electrode
BH 3	0.960	0.904
	.960	.904
	.950	.894
BH 4	.970	.914
	.965	.909
	.962	.906
	.960	.904
	.970	.914
BH 5	.970	.914
	.965	.909
	.960	.904
	.950	.894
Average Value	0.962	0.906
Average Deviation	0.005	0.005

standard hydrogen electrode, and the average deviation was ±0.005 v. The measured potentials remained within the limits of 0.894 and 0.914 v, even after the anodes sustained current drains for 1-1/2 hr at 100 ma/cm^2. These limits are considered satisfactory for a reasonable degree of constancy and reproducibility.

As shown in Fig. 4, the open-circuit potential of a typical anode in a recently operated fuel cell was measured as 0.907 v, initially, and as 0.824 v after continuous operation at 70 ma/cm^2 for 2 weeks. It is possible that the anode was gradually poisoned by trace quantities of catalyst from the cathode, since the anode and cathode were immersed in the same electrolyte. The data indicate that the drift toward lower open-circuit potentials was essentially complete after the first 2 days of rapid decline.

The anode half-cell reaction may be expressed as follows:

$$N_2H_4\,(aq) \; + \; 4\,OH^-\,(aq) \; = \; N_2\,(g) \; + \; 4\,H_2O\,(l) \; + \; 4\,e^- \qquad (1)$$
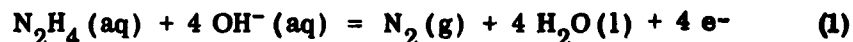
The standard oxidation potential E° is 1.16 v (Ref. 1). If a correction is made by applying the Nernst equation and the activity of KOH in 30-percent KOH, the half-cell oxidation potential is calculated to be 1.21 v. This appreciable rise in the potential is caused by the exceptionally high activity of KOH under the conditions of the experiment (Ref. 3). The KOH concentration of the electrolyte utilized may be represented as follows:

<u>30-percent KOH, 25°C (6.90 molar, 7.64 molal)</u>

$$\text{Activity coefficient} \; = \; 3.40$$
$$\text{Activity of KOH} \; = \; 25.97 \text{ molal}$$
$$\text{Geometric mean, "OH}^- \text{ activity"} \; = \; 5.10 \text{ molal}$$

It appears, therefore, that more than 0.3 v of the open-circuit potential is lost in practice. This discrepancy between the observed and theoretical values has been investigated by Pavela (Ref. 4), who found that "platinized platinum immersed in a solution of hydrazine acquires a potential corresponding to the reversible hydrogen potential at low pressure" and that "the hydrogen pressure varies with pH, increasing approximately as the third power of the hydroxide ion concentration."

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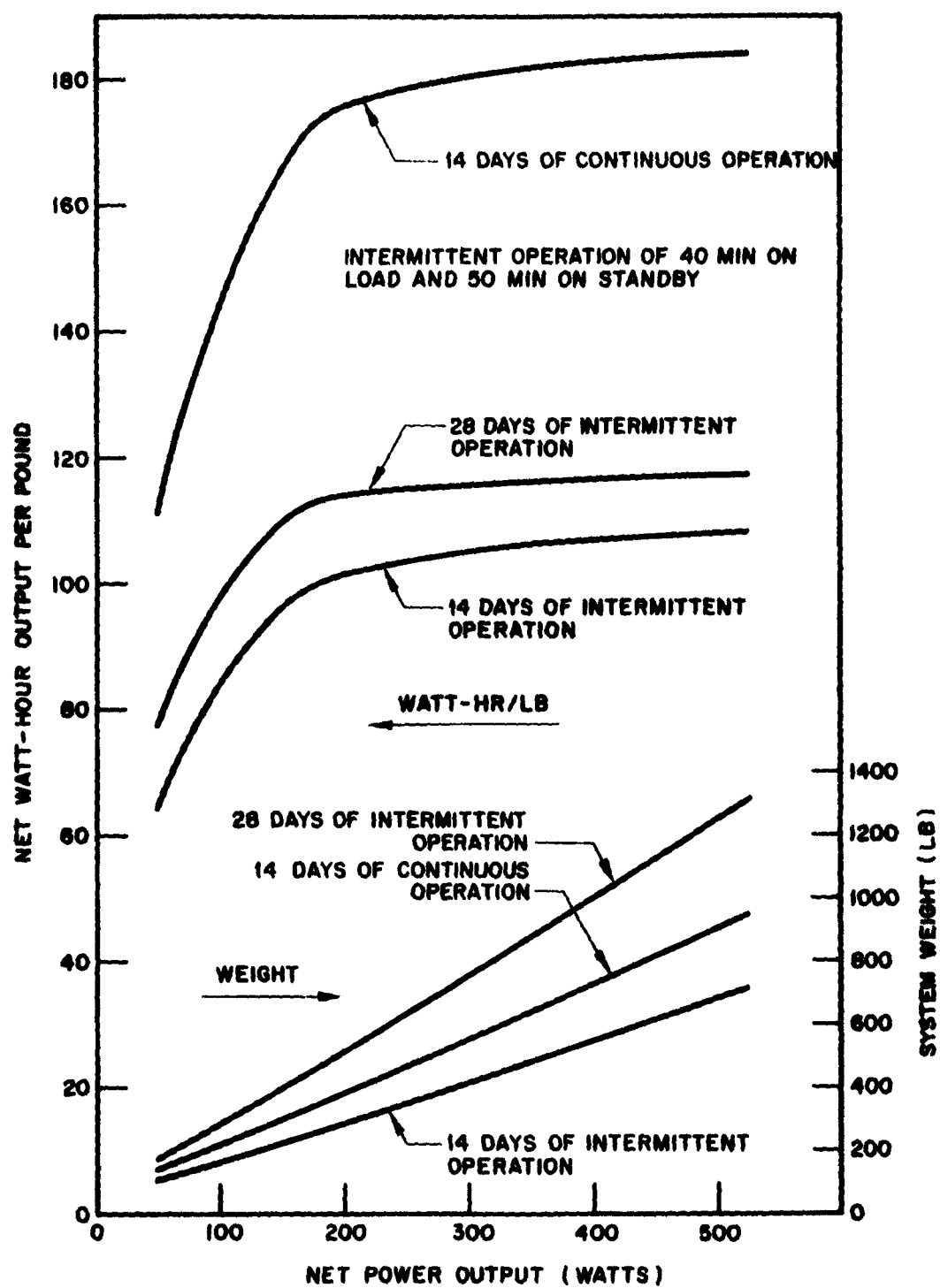
Fig. 4 Average Operational Electrochemical Characteristics of an LMSC Hydrazine-Oxygen Fuel Cell

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In the experiment conducted for the present study, hydrazine decomposed spontaneously into two parts hydrogen and one part nitrogen at a rate of total gas evolution of about 1×10^{-3} ml (STP)/sec. The presence of hydrogen thus seems assured, at least at open circuit. The external electrode pressure is about 1 atm, and the hydrogen partial pressure at the anode is expected to be about 2/3 atm.

The anode half-cell reaction for hydrogen may be expressed as follows:

$$H_2(g) + 2 OH^-(aq) = 2 H_2O(l) + 2 e^- \tag{2}$$
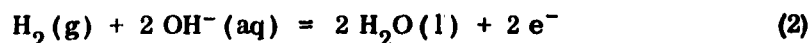
The standard oxidation potential E° is 0.828 v (Ref. 1). If a correction is made, as before, by applying the Nernst equation and the activity of KOH in 30-percent KOH, the half-cell oxidation potential is calculated to be 0.870 v at 2/3 atm of hydrogen pressure.

The summarized results of this discussion (Table 2) show that the observed values are considerably closer to the estimated hydrogen potential than to the hydrazine potential. Based on the assumptions of the foregoing calculations, the experimental agreement of the measured open-circuit potential with the hydrogen potential is considered to be close and provides a valuable clue in the determination of the mechanism of the anodic hydrazine oxidation. The spontaneous decomposition into a 1:2 ratio of nitrogen to hydrogen also provides direct evidence for the assumption of a "hydrogen electrode" mechanism.

Table 2

HYDRAZINE AND HYDROGEN OPEN-CIRCUIT POTENTIALS IN 6.90 M KOH
AT 25°C WITH BLACK PLATINUM, POROUS NICKEL ANODES,
HEAT TREATED AT 300°C
(In volts versus standard hydrogen electrode)

Estimated Hydrogen Potential, 0.67-atm Pressure	Theoretical Hydrazine Potential, 0.2 M	Observed Hydrazine Potential, 0.2 M With 2-Week-Old-Anodes	Observed Hydrazine Potential, 0.2 M With Fresh Anodes
0.865	1.21	0.824	0.906

Polarization characteristics. The polarization characteristics of some representative hydrazine anodes at 50° and 25°C, respectively, are shown in Figs. 4 and 5. In Fig. 4, polarization is shown both before and after a 2-week run at 70 ma/cm^2. The performance was observed to remain essentially constant after 2 to 3 days of the run. Because of this constancy, the hydrazine anode is considered promising for application to fuel cell battery operation.

Figure 5 shows the results of preparing two groups of anodes by different methods. One group was sintered at 400°C, rather than the usual 300°C, and the other group was not sintered. The sintering is seen to cause a decrease in electrochemical performance or an increase in the polarization at a given current density. Furthermore, the higher the temperature of sintering, the greater the effect. The open-circuit potential, however, remained practically unaffected. Similar sintering was accomplished in earlier experiments with ammonia (Ref. 2).

A possible explanation of these effects is that the active catalyst sites or contributing surface areas are partially destroyed by the sintering or heating process. It has been shown that the black platinum surface area is lost in a regular way by sintering in hydrogen at elevated temperatures (Ref. 2).

The use of sintered anodes, at various degrees of area loss, presents a novel method of theoretical import for varying the number of active catalyst sites available during current drains. It has also been suggested that known trace quantities of selective catalyst poisons may be used in this connection (Ref. 5).

The polarization runs were made by recording the current density and anode voltage versus a Hg-HgO (30-percent KOH) reference cell. The run was started with an open-circuit reading; during the run, each current setting exceeded the previous one. After considerable polarization — in excess of 0.3 v — was obtained, the current settings were decreased until an open-circuit reading was again recorded. It is important to wait a short time, usually less than 5 min, after a given current value is set in order

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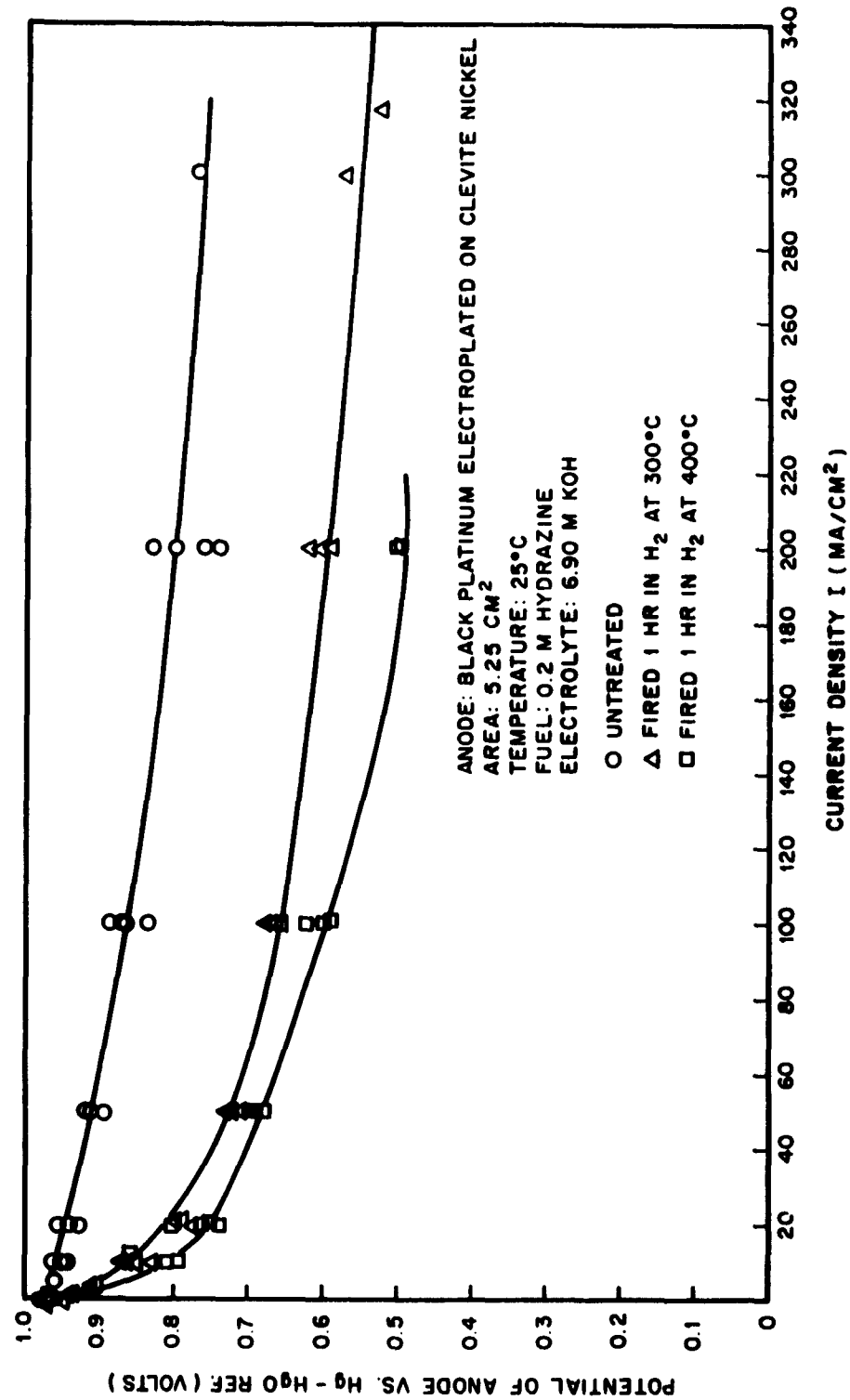
Fig. 5 Modification of Electrochemical Characteristics of Heat-Treated Black Platinum Anodes in Hydrazine Anodic Oxidation

to achieve a "steady state." The constancy, usually within 5 mv, is checked by a second reading at the given setting about 2 min after the first reading.

For the half-cell experiments (Fig. 5), the current was impressed upon the system, between the anode and cathode, from lead-acid batteries, and was regulated by resistors. Thus, the anode was subjected to the same conditions in electrolysis as in fuel-cell operation; in practice, no difference in performance was observed.

Concentration variation runs. The result of varying the hydrazine concentration from 0.001 to 0.2 M is shown in Fig. 6. The polarization curve is steadily improved as the hydrazine concentration is increased, but the improvement from 0.1 to 0.2 M is not very great. When a more concentrated hydrazine (e.g., 3 M) was used, the hydrazine rapidly decomposed spontaneously at the anode surface. Therefore, the 0.2-M concentration is considered to be the upper limit for maintaining good coulombic efficiency in alkaline solution. The dependence of open-circuit potential upon concentration was not obtained accurately enough for application of the Nernst equation to Eq. (1). However, the data summarized in Table 3 indicate the order of magnitude of the dependence and the scope required for more precise work.

Table 3

OPEN-CIRCUIT POTENTIALS OF HYDRAZINE
SOLUTIONS IN 6.90 M KOH AT 25°C

Open-Circuit Potential Vs. Std. H_2 Electrode (volts)	Hydrazine Concentration (moles/liter)
0.60	0
.71	0.000100
.84	.00100
.88	.0100
.90	.100
.90	.200

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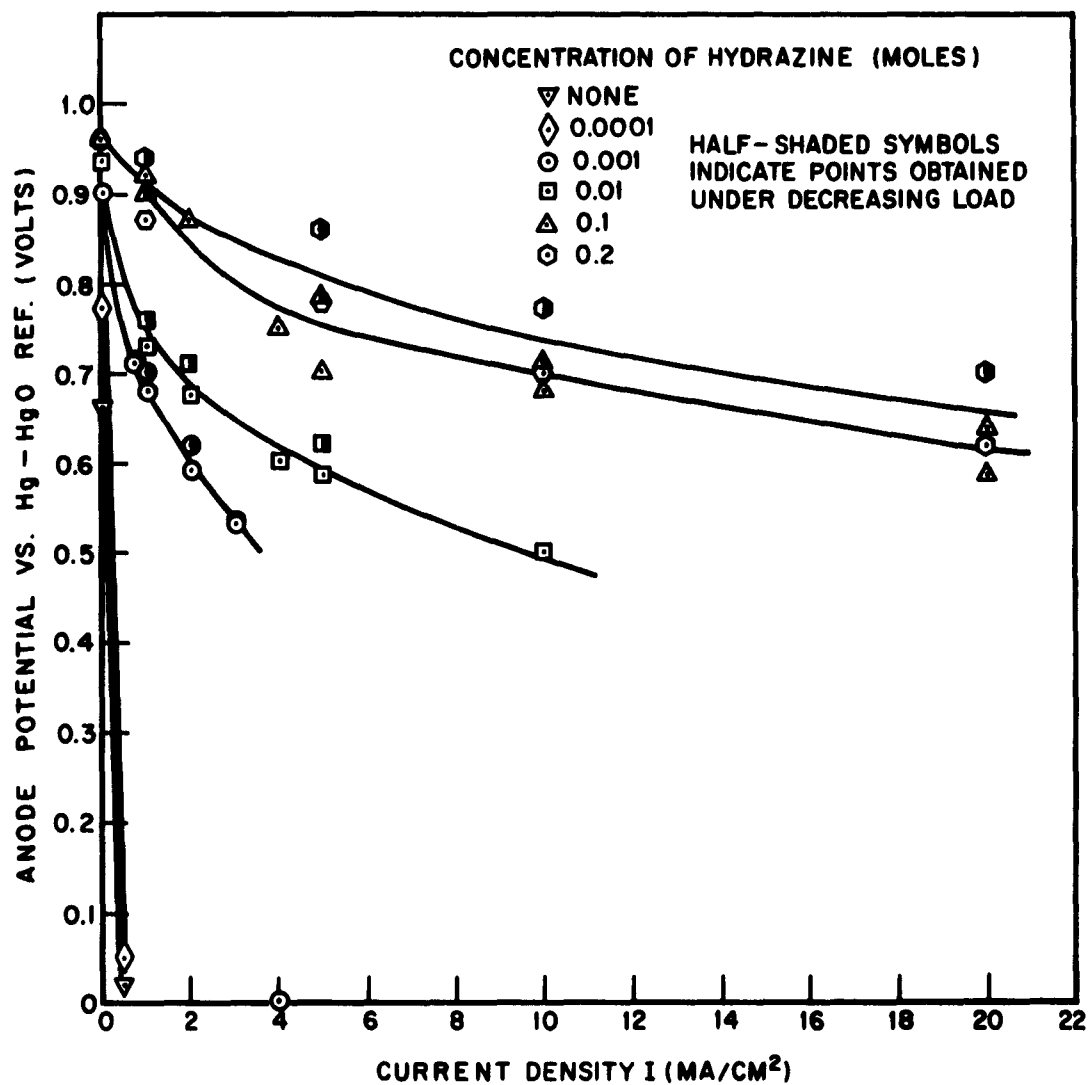
Fig. 6 Polarization Characteristics of the Hydrazine Anode With Different
Hydrazine Concentrations in 30-Percent KOH

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2.1.2 Spontaneous Decomposition

The contribution of spontaneous decomposition to hydrazine loss could be of considerable importance in an operational system. Therefore, an effort was made to determine the extent of the contribution of the decomposition to the incomplete electrochemical oxidation of hydrazine in the hydrazine-oxygen fuel cell batteries which were previously tested.

Small anodes, 3 × 3 cm, were left on open circuit in 0.2 M hydrazine, 30-percent KOH, at 25°C, and the gas evolved was measured as a function of time. One set of anodes was washed and stored in distilled water, while another set was stored in the hydrazine solution. The evolved gas was analyzed, using a gas chromatographic unit.

Some of the results of this experimental work are listed in Table 4. The effect of catalytic activity on the rate of spontaneous decomposition is seen to be slightly decreased by water storage, but storage in 0.2 M hydrazine, 30-percent KOH, renders the catalyst less effective by factors of 10 or more. The table also presents an order of magnitude of correction which can be applied for estimates in the hydrazine fuel cell development work.

Table 4

RATE OF TOTAL GAS EVOLUTION FROM A 0.2 M HYDRAZINE, 6.90 M KOH
SOLUTION EXPOSED TO A 3 × 3-CM BLACK PLATINUM ANODE,
HEAT TREATED AS INDICATED, AT 22°C

Treatment of Black Pt. Anode	Solution in Which Immersed	Catalyst Number	Rates in cc (STP)/sec After Immersion in Solution				
			0 Day	1 Day	2 Days	4 Days	19 Days
Unfired	N_2H_4, KOH	CR1	0.187	0.0089	0.0056		0.0036
	H_2O	CR2	.171	.1120	.0745		.0945
H_2 Fired 1 hr, 300°C	N_2H_4, KOH	CR3	.0516	.0032	.0022		.0028
	H_2O	CR4	.0560	.0346	.0183		.0425
H_2 Fired 1 hr, 400°C	N_2H_4, KOH	CR5	.0276	.0012		0.0011	
	H_2O	CR6	.0249	.0089		.0079	

The sintering of black platinum was also found to reduce its activity with respect to hydrazine decomposition. Figure 7 is a plot of the temperature of black platinum heat treatment as a function of the initial rate of decomposition. The decrease in activity may be directly related to the loss of surface area of the catalyst. Figure 8 is a typical curve of the rate of decomposition.

An analysis of the evolved gases showed that only nitrogen and hydrogen were present, in a 1:2 ratio. This implies the following stoichiometry:

$$N_2H_4(aq) = N_2(g) + 2H_2(g) \tag{3}$$
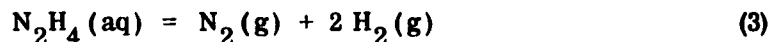
This path of decomposition, without ammonia formation, can be expected at the high pH's employed, according to Gutbier and Neundlinger (Ref. 6).

2.1.3 Hydrazine Anodic Oxidation

Both the formation of hydrogen at the anode and the hydrazine open-circuit potential suggest that the anodic oxidation occurs through hydrogen as an intermediate. The work of Pavela (Ref. 4) further supports this possibility. A probable sequence of reactions, not necessarily elementary, is as follows:

$$N_2H_4(aq) \rightarrow N_2H_4(ads) \tag{4}$$

and then, on the surface of the anode,

$$N_2H_4 = N_2 + 4H \tag{5}$$

$$H \rightarrow H^+ + e^- \tag{6}$$

$$OH^- + H^+ \rightarrow H_2O \tag{7}$$

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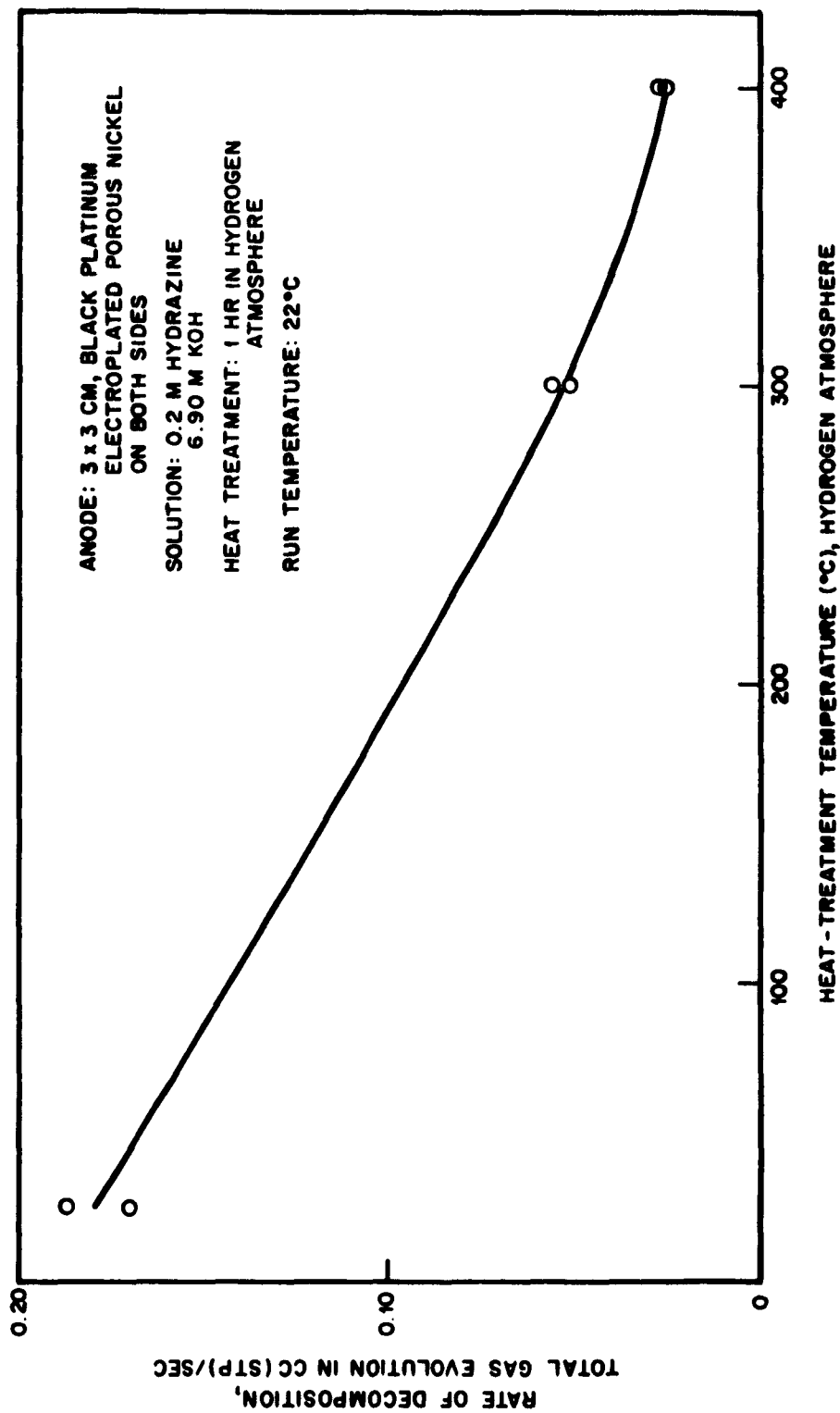
Fig. 7 Modification in the Rate of Spontaneous Decomposition of Hydrazine in Alkaline Solution by Heat-Treated Black Platinum Anodes

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CATALYST: BLACK PLATINUM
MATRIX: 0.032 - IN. CLEVITE NICKEL, 3 x 3 CM
DEPOSITION: ELECTROPLATED
TREATMENT: H_2 FIRED 1 HR AT 400°C
TIME IN 0.2 M N_2H_4, 6.90 M KOH SOLUTION: 1 DAY

CATALYST TEMPERATURE: 22.0°C
PRESSURE: 770.5 MM Hg
AREA: 18 CM^2
WEIGHT: 112.5 MG
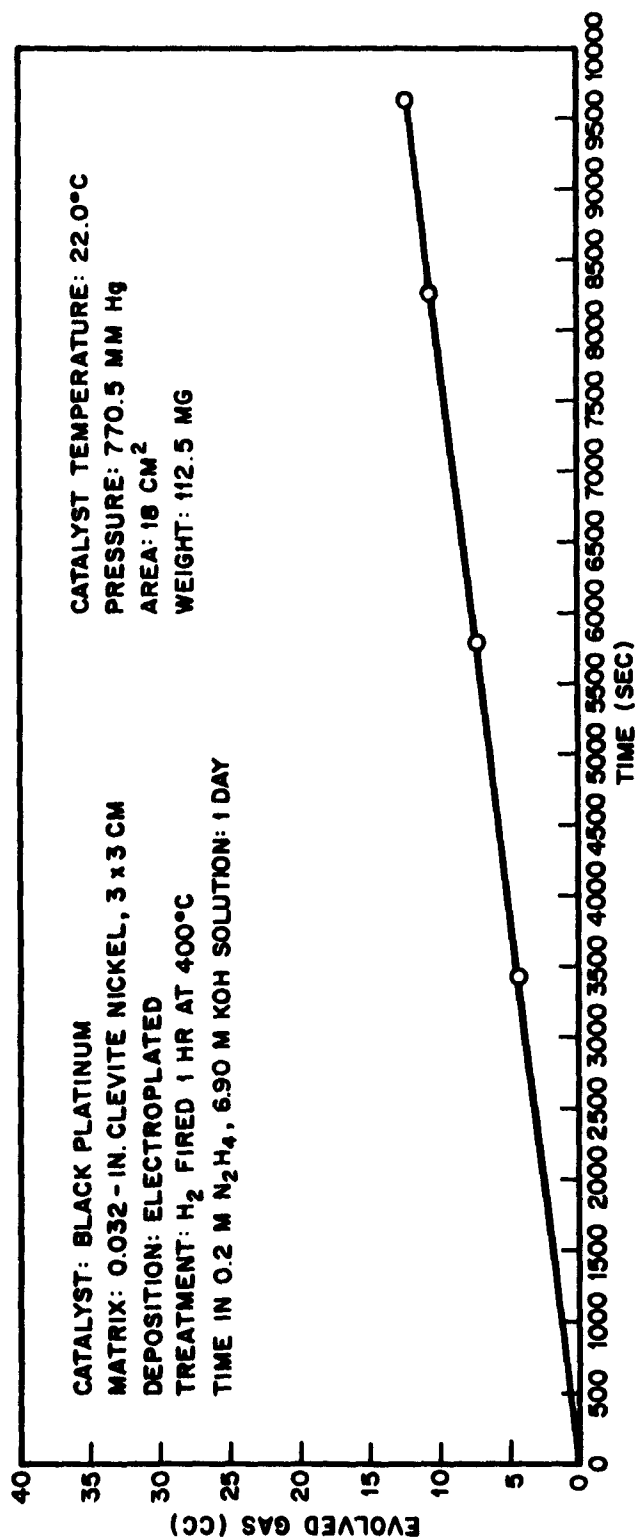
Fig. 8 Typical Results for the Spontaneous Decomposition of Hydrazine in Alkaline Solution

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2.1.4 Coulombic Efficiency Runs

A eudiometer-gas separator (Fig. 3) was used to perform the coulombic efficiency runs. Gas chromatographic analyses were made on the samples of the collected anode gas.

The results of the coulombic efficiency experiments are summarized in Table 5. It appears that the coulombic efficiency remains within a few percent of 100 percent if the ratio of cathode to anode gas is considered together with the anode gas analysis. This high efficiency with isolated anodes suggested that the 50- to 70-percent efficiency obtained with fuel cell batteries is the result of hydrazine loss at the cathode by direct chemical oxidation by oxygen. The heat of this oxygen reaction is also known to diminish appreciably the overall life of the carbon cathodes currently used.

The presence of a small amount of hydrogen in the anode gas was found to be higher with the unsintered anodes than with the sintered anodes (Table 5). This amount of hydrogen indicates that spontaneous decomposition and electrochemical oxidation occur simultaneously and that the reaction expressed by Eq. (6) does not necessarily consume all the hydrogen that is formed. A tentative explanation is that reactions which compete with the reaction of Eq. (6) occur, involving the formation and desorption of molecular hydrogen.

The problem of practical optimization is to evaluate the importance of polarization and coulombic efficiency. In this case of hydrazine, the best catalyst from the standpoint of polarization is the worst from the standpoint of coulombic efficiency because of the occurrence of spontaneous decomposition losses.

Table 5

A SUMMARY OF THE HYDRAZINE ANODE COULOMBIC EFFICIENCY RUNS[a]
(Solution: 0.2 M Hydrazine, 6.90 M KOH. Temperature: approximately 22°C.)

Anode No.	Polarization Run No.	Firing Temp (°C) [b]	Spontaneous Decomposition Rate (10⁻³ ml/sec)	Coulombic Efficiency: Ratio of Cathode to Anode Gas	I for Coulombic Efficiency Measurement (ma/cm²)	I at 0.2 v Polarization (ma/cm²)	Anode Gas (%) During Efficiency Runs N₂	H₂	Open-Circuit Potential Vs. Hg-HgO (volts)
BH 1 BH 2		Gas-liquid separator was not satisfactory for runs on these anodes							
BH 3	H3a	300°C		2.05	50	16	95.1	4.9	0.950
				2.01	50				
				2.06	50		97.2	2.8	
BH 4		300°C	1.13	2.26	50				
			1.03	2.06	50				
			1.05	2.02	50				
				2.08	50				
BH 5	H5a	300°C	3.36	2.02	50	28.5			0.970
	H5b		2.60	2.05	50	26.5			0.955
				1.96	100				
				1.93	100				
				2.12	100		99.1	0.9	
BH 6	H6a	400°C	3.45	1.95	50	20.0			0.960
	H6b		2.49	1.92	50	33.0			0.960
				1.92	50				
				1.93	50				
				1.87	50		97.1	2.9	
BH 7	H7a	400°C	3.46	2.15	50	17.5			0.960
	H7b		1.97	2.10	100	45.0			0.960
	H7c			2.15	50	29.0			0.965
				2.10	100				
				2.14	100		98.8	1.2	
BH 8		R.T.	11.95	1.71	50				
	H8b			2.02	100	185.0	93.2	6.2	0.970
	H8c					115.0			0.970
	H8d					185.0			0.875
BH 9	H9a	R.T.	14.9	1.99	100	300	93.4	6.6	0.970
	H9b		12.2[c]	2.12	100	28			0.960
			6.0						
Cat. 2		R.T.	Static, Not Flow-Through[d]						

(a) Anode: black platinum electroplated on Clevite nickel and H₂.
(b) Duration of firing: 1 hr.
(c) Anode gas during spontaneous decomposition: 33.4% N₂, 66.6% H₂.
(d) Anode gas during spontaneous decomposition: 33.2% N₂, 66.8% H₂.

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2.1.5 Multiple Cells

The results of experiments on the latest multiple-cell hydrazine-oxygen fuel cell are summarized in Fig. 4. These performance characteristics can be used as the basis for tentative estimates for larger units. Figure 2 of the first quarterly report (Ref. 7) shows the experimental apparatus employed in the operation of such a multiple unit.

The 1000-hr life span of these batteries is limited by the cathode life, and hydrazine is known to deteriorate pressed carbon cathodes. Eventual wetting-through of the cathode floods the battery. However, the presence of hydrazine in the electrolyte has been found to have a beneficial effect on the electrochemical performance of the pressed carbon oxygen cathode. The determination of the factors involved in this effect is a possible subject of future study.

The coulombic efficiency of the multiple-cell battery has already been discussed. It should be noted that the shunt currents with the 5-cell fuel cell battery of Fig. 4 were found to be less than 2 ma/cm^2. This battery employs an LMSC radial feeding design.

2.2 FORMALDEHYDE ANODE IN ALKALINE SOLUTION

2.2.1 Electrochemical Characteristics

The apparatus described in subsection 2.1.1 was used in this work, except that the anode was a platinized platinum screen.

For an anode consisting of 1.0 M formaldehyde and 40-percent potassium carbonate, the average observed anode potential was 0.70 versus a Hg-HgO reference. Other platinized platinum anodes gave typical values up to 0.78 v at open circuit.

Figure 9 shows the effect of current drain on the anode potential. It was found that the anode would give reproducible polarization after remaining immersed in the fuel
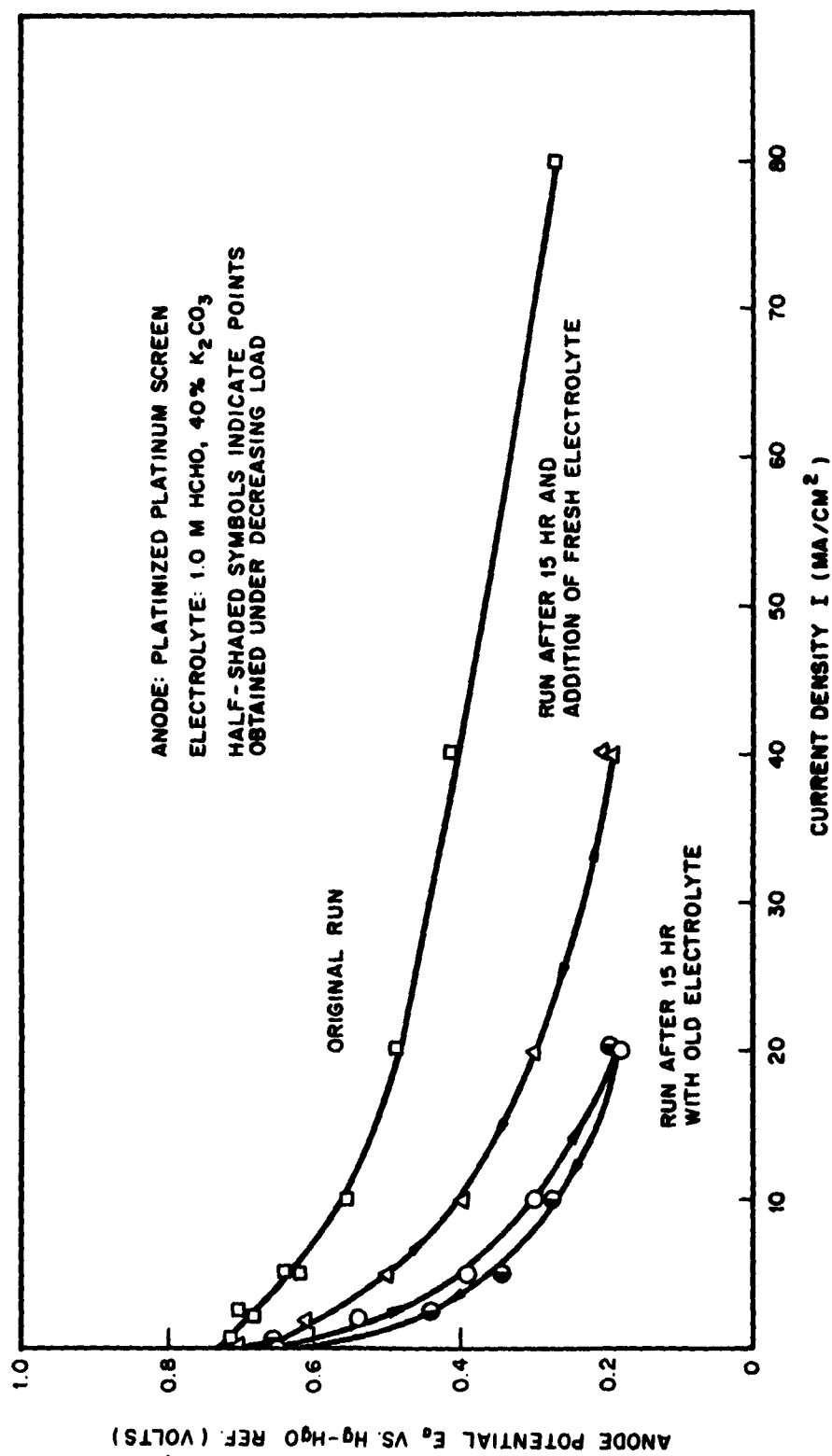
Fig. 9 Loss in Activity of the Formaldehyde Anode After 15 hr at 20 ma/cm²

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electrolyte for several days at open circuit. However, when 20 ma/cm^2 are impressed for 15 hr, the polarization characteristics are markedly changed. When fresh electrolyte fuel is introduced, the original polarization characteristics are approached.

2.2.2 Anode Poison Studies

A tentative explanation of the behavior just described is that a "poison" is being generated as a side-reaction or end-reaction product during the anodic oxidation of formaldehyde. As a test of this hypothesis, several possible "poisons" were added to the 1.0 M formaldehyde, 40-percent potassium carbonate electrolyte. The polarization characteristics were found to be only slightly affected by 1 M fructose, 1 M sorbose, and 0.5 M potassium formate.

Using the hypothesis that the electrochemical reaction generated products similar to those which are formed when formaldehyde reacts with itself in alkaline solution (Ref. 8), the following experiment was performed: A 15-percent solution of formaldehyde in 40-percent potassium carbonate was heated at 90°C for several hours until a light-brown coloration was formed. About 3 grams of this product, probably a formose (Ref. 8), were added to 500 ml of the fuel electrolyte. Figure 10 shows the marked poisoning effect of this product.

The self-poisoning exhibited by the formaldehyde anode with continued current drain indicates that more study is required if alkaline side operation is eventually to be used. Improvement of anode catalysis is a possible solution to the problem.

2.2.3 Concentration Variation

The results of varying the formaldehyde concentration are plotted for anode potential versus current density in Fig. 11. It is seen that the polarization characteristics are generally poor for low concentrations of formaldehyde and that concentrations of 0.1 M and 1.0 M are required to improve the performance.
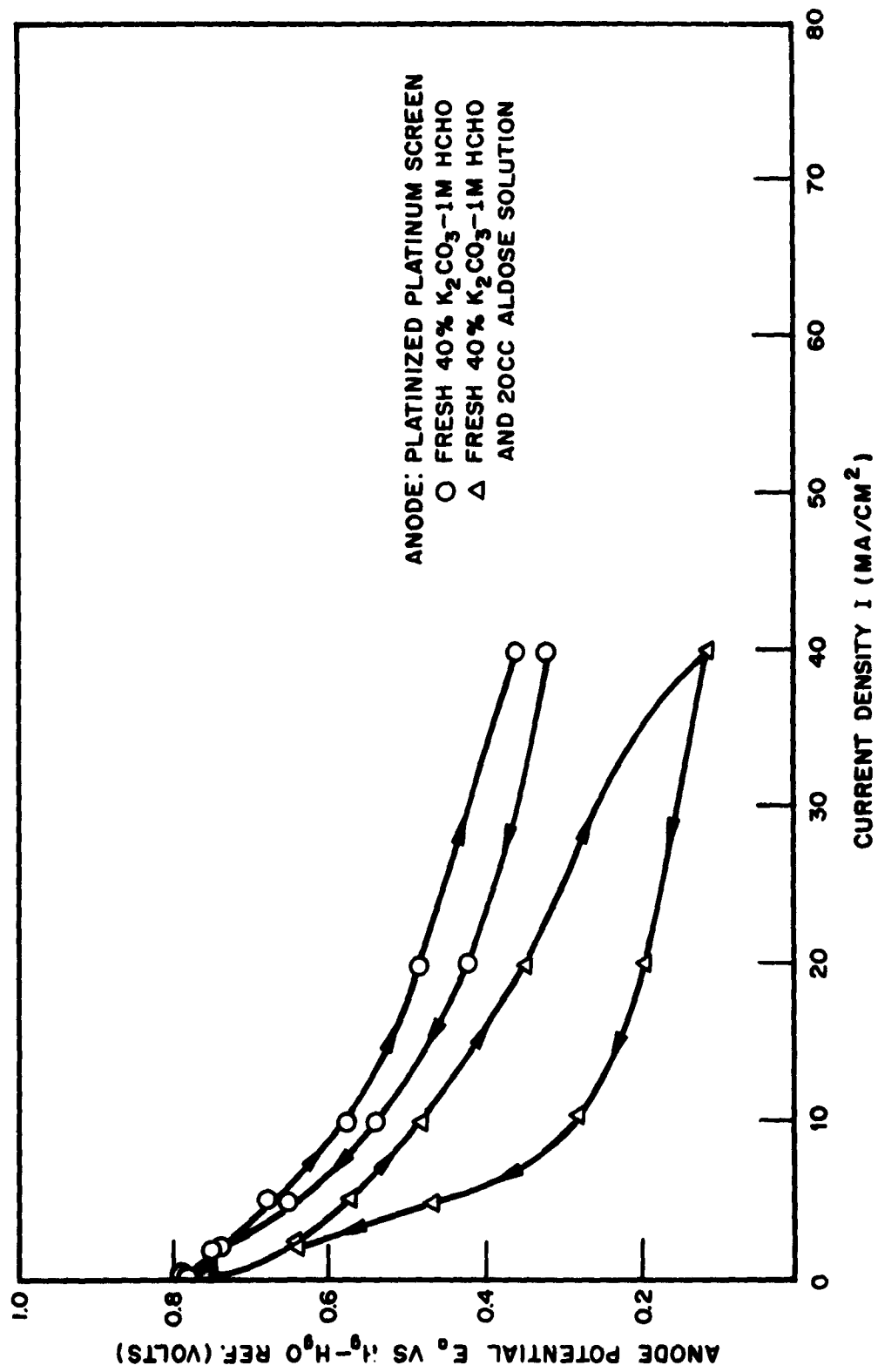
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Fig. 10 Effect of Small Amounts of Aldose–Type Product on the Polarization Characteristics of the Formaldehyde Anode
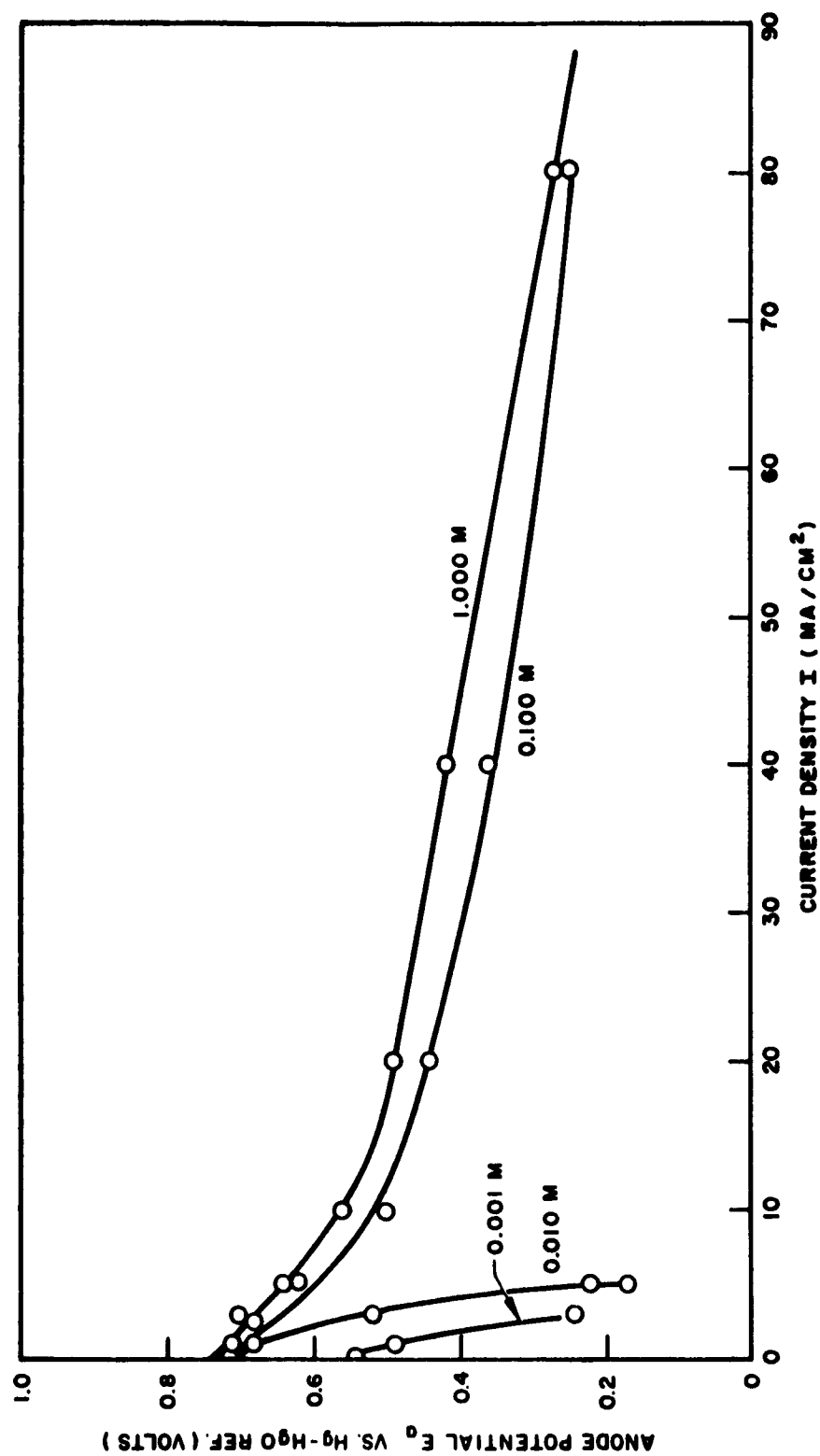
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Fig. 11 Polarization Characteristics of the Formaldehyde Anode With Different Formaldehyde Concentrations in 40-Percent K_2CO_3

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2.3 AMMONIA ANODE AT INTERMEDIATE TEMPERATURES

Work on the ammonia anode has continued. Figures 12, 13, and 14, respectively, show the following results of the most recent work: (1) the potential-current characteristics of a typical ammonia-oxygen fuel cell, (2) the cell performance change with time, and (3) the potential-current characteristics of a large number of individual cells on one graph. These data may be useful for future optimization calculations.

The primary problem of this system has been the slow but steady loss of cell performance with operation time, as shown in Fig. 13. The occurrence of an irreversible change in the electrolyte of hydroxide ion to nitrite and nitrate ion is tentatively considered to be the reason for this poor cell life.

Analysis of the electrolyte for nitrate and nitrite ion content by standard titrametric methods (Ref. 9) yielded the data of Table 6. After a cell was run for 13.7 amp-hr (2 days), a thin slice of electrolyte near the anode was much richer in nitrate and nitrite ion than a corresponding slice from the cathode side. The body of the electrolyte contained an intermediate ion concentration of nitrate and nitrite. This evidence suggests that incomplete electrochemical oxidation of the ammonia occurs at the anode, according to the following half reactions:

$$NH_3 + 9\ OH^- = NO_3^- + 6\ H_2O + 8\ e^- \tag{8}$$

$$NH_3 + 7\ OH^- = NO_2^- + 5\ H_2O + 6\ e^- \tag{9}$$
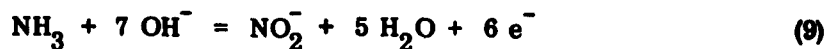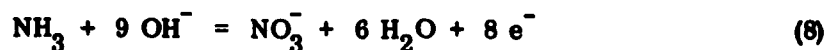
An experiment was designed to determine whether direct oxidation of ammonia with oxygen at the cathode would result in nitrite-nitrate formation. This experiment was performed by electrolyzing a cell from an external direct-current source for about 1 week at 10 ma/cm^2. Only ammonia gas was permitted to contact the electrolyte cake on both the cathode and the anode sides. Nitrate and nitrite ion were again found on the anode side, in approximately the same ratio as in the previous experiment. These results eliminate the possibility of a direct chemical reaction between ammonia

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Table 6

ANALYTICAL RESULTS FOR NITRATE-NITRITE FORMATION IN AN INTERMEDIATE-TEMPERATURE AMMONIA-OXYGEN FUEL CELL AFTER 2 DAYS OF CONTINUOUS OPERATION

Constituent	Quantities Found (moles)				NO_2^- and NO_3^- in Equivalents
	Near Anode	In Center	Near Cathode	Total	
OH^-	0.0718	0.249	0.0523	0.373	
NO_2^-	0.0131	0.00364	0.00031	0.0171	0.103
NO_3^-	0.00452	0.00465	0.00230	0.0115	0.0918

NOTES:
Total equivalents: 0.195.
Total electrons drawn from cell: 0.505 equivalents.
Total electrons used in NO_3^- and NO_2^- formation: 0.195 equivalents.

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CELL: NO. 12
SYSTEM: INTERMEDIATE-TEMPERATURE AMMONIA-OXYGEN FUEL CELL
ANODE: BLACK PLATINUM ON CLEVITE NICKEL, KEL-F WET-PROOFING TREATMENT
CATHODE: FLAKE SILVER ON CLEVITE NICKEL BACKING
ELECTROLYTE: Na-K-Li-Ca(OH)$_2$, 39.7: 30.2: 5.8: 14.6 (H$_2$O, 14.6) % BY WT
ELECTROLYTE DISC SURFACE AREA: 22.7 CM^2
TEMPERATURE: 143°C
PRESSURE: CIRCA 10-IN. WATER GAGE

iR

V$_c$

ΔE$_c$

ΔE$_a$

CURRENT DENSITY I (MA/CM^2)

POTENTIAL (VOLTS)

Fig. 12 Potential-Current Characteristics of Intermediate-Temperature Ammonia-Oxygen Fuel Cell

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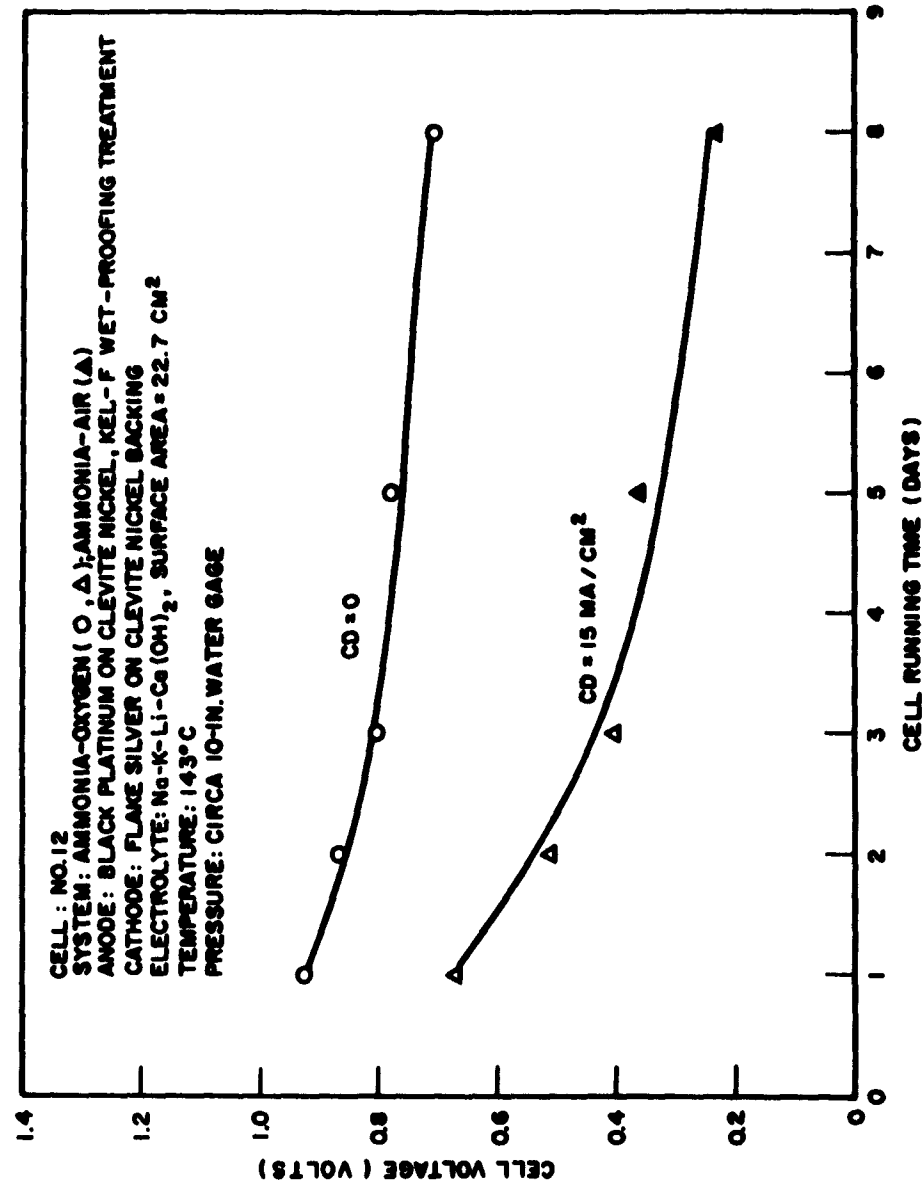
Fig. 13 Cell Performance Change With Time, Ammonia-Oxygen Fuel Cell

CELL: NO.12
SYSTEM: AMMONIA-OXYGEN (O , △);AMMONIA-AIR (▲)
ANODE: BLACK PLATINUM ON CLEVITE NICKEL, KEL-F WET-PROOFING TREATMENT
CATHODE: FLAKE SILVER ON CLEVITE NICKEL BACKING
ELECTROLYTE: Na-K-Li-Ca(OH)$_2$, SURFACE AREA = 22.7 CM^2
TEMPERATURE: 143°C
PRESSURE: CIRCA 10-IN. WATER GAGE

CD = 0

CD = 15 MA/CM^2

CELL RUNNING TIME (DAYS)

CELL VOLTAGE (VOLTS)

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SYSTEM: AMMONIA - OXYGEN
ANODE: BLACK PLATINUM ON CLEVITE NICKEL, KEL—F WET—PROOFING TREATMENT
CATHODE: FLAKE SILVER ON CLEVITE NICKEL OR SINTERED SILVER BACKING
ELECTROLYTE: Na – K – Li – Ca (OH)$_2$
TEMPERATURE: 136° - 145° C
PRESSURE: CIRCA 10-IN. WATER GAGE

Fig. 14 Voltage–Current Density Characteristics of Several Typical Ammonia–Oxygen Fuel Cells

O CELL NO. 12
◇ CELL NO. 14
△ CELL NO. 15
□ CELL NO. 19

HALF—SHADED SYMBOLS INDICATE POINTS
OBTAINED UNDER DECREASING LOAD

CURRENT DENSITY I (MA/CM^2)

CELL VOLTAGE V$_c$ (VOLTS)

and oxygen at the anode, with consequent nitrate and nitrite formation, which presumably could occur because of leakage of oxygen gas through the electrolyte disc to the anode. Since the formation of nitrate and nitrite is more definitely established as a possible reason for poor cell life, a serious problem in future experiments will be the selection of more suitable electrolyte mixtures and catalysts.

The generation of nitrate and nitrite ion from ammonia-oxygen cells which use molten caustic electrolytes was reported by Marie and Haenny (Refs. 10 and 11).

2.4 AQUEOUS AMMONIA ANODE

The performance of the ammonia-oxygen fuel cell anode was reported in the last quarterly report (Ref. 12). The anode continued to maintain the reported electrochemical characteristics. The run was discontinued on 19 January 1962; the total time of the run was more than 6 months. Periodic additions of trace amounts of hydrazine to the ammonia electrolyte are believed to be responsible for the indefinite life found.

2.5 CATHODE STUDIES

2.5.1 Metal Cathodes

Work is continuing on the fabrication of all-metal cathodes. Fabrication techniques involve work on a double porosity structure. For alkaline electrolytes, a fine layer of a mixture of nickel and Raney silver powder is sintered to a coarse matrix prepared from nickel powder. The resulting porous-metal electrode is then leached according to methods outlined by Justi and others (Ref. 13).

Some of the preliminary data on the pressed metal cathodes are given in Fig. 15. The effect of the variation of oxygen pressure from 9.3 to 15.9 psi is shown with respect to the potential-current characteristics of the cathode. Also shown is one measurement employing air at 8.5 psi. These preliminary results may be considerably improved by using (1) more uniform particles in cathode fabrication, and (2) other active Raney alloys.
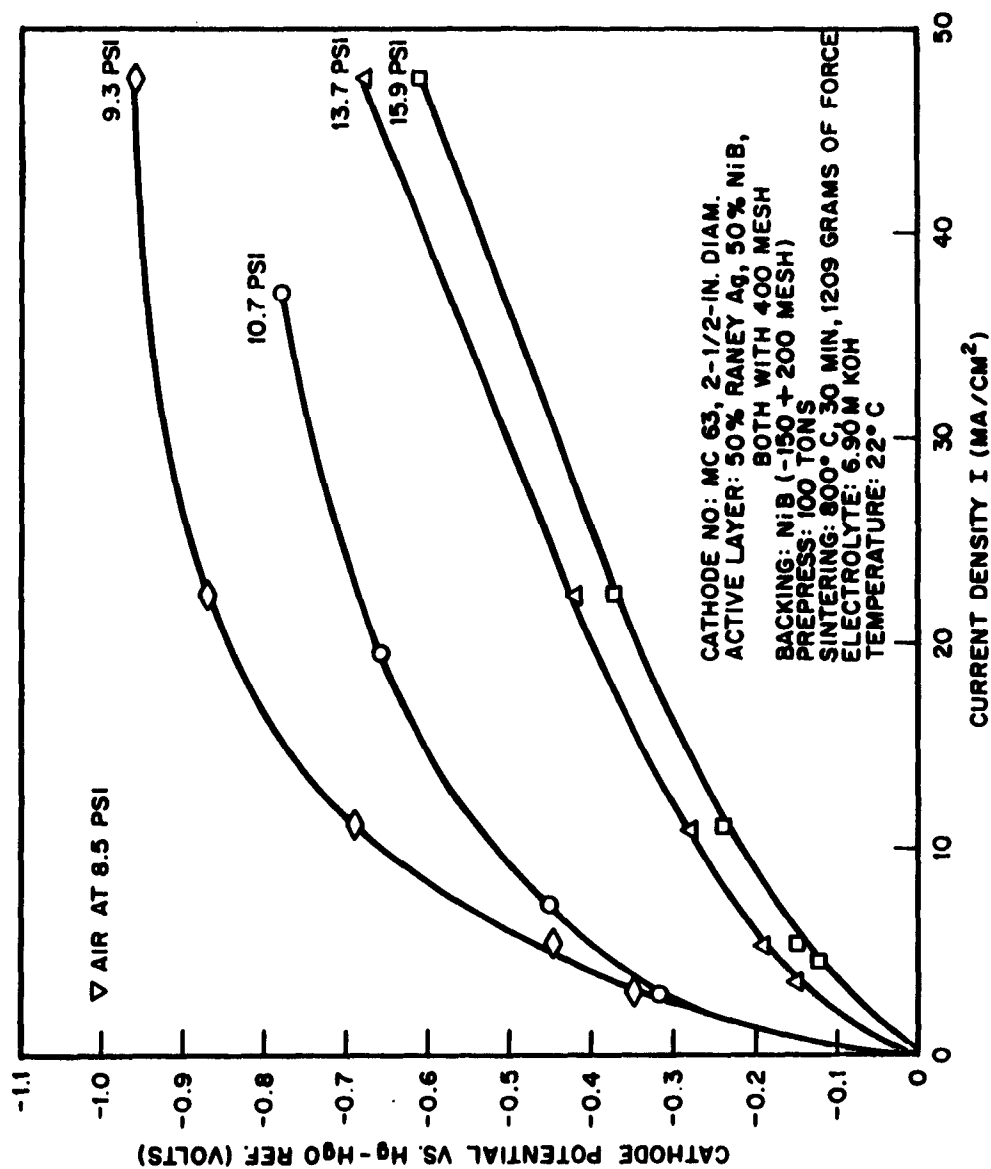
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Fig. 15 Effect of Oxygen Pressure on the Electrochemical Characteristics of an All-Metal Oxygen Cathode

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The fabricated cathodes were found to be nonuniform by means of a series of bubble pressure tests, and techniques for obtaining narrower cuts in the size distribution of fine particles are being studied.

A Haultain Infrasizer, manufactured by Infrasizer Limited, Toronto, Canada, is now being used for fractionating particles in the 10- to 80-μ size range.

2.5.2 Pressed Carbon Cathodes

The typical results of oxygen and air oxidants with LMSC pressed carbon cathodes are listed in Table 7. The data indicate the electrochemical performances which can now be expected in applications with larger fuel cell units. The proprietary catalyst used in these 4-in. cathodes is attacked by acid electrolyte; therefore, the cathodes are limited to use in alkaline media. The present life span of the pressed carbon cathodes is about 1000 hr (as stated in subsection 2.1.5). With the development of stronger, temperature-resistant binders, improvement of cathode life is expected.

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Table 7

A COMPARISON OF THE RESULTS WITH OXYGEN AND AIR IN A MULTIPLE-CELL, HYDRAZINE FUEL CELL BATTERY(a)

Cell No.	Open-Circuit Potential Oxygen		Closed-Circuit Potential			
			21.8 ma/cm² Oxygen		21.0 ma/cm² Air	
	Cell Voltage(b)	Cathode Potential(c)	Cell Voltage	Cathode Potential	Cell Voltage	Cathode Potential
1	0.76	0.12	0.36	0.08	0.16	0.24
2	.75	.14	.58	.11	.31	.40
3	.75	.10	.58	.10	.33	.33
4	.85	.15	.95	–	.78	.22

(a) Number of cells: Five
Solution: 0.2 M hydrazine, 6.90 M KOH.
Run temperature: 43°C.
Pressure differential across cathode: 0.8 in. Hg.
Cathode gas pressure: 37 in. of water.
Cathodes: Pressed carbon.

(b) In all cases, cell voltage is expressed in volts.
(c) In all cases, cathode potential is expressed in volts versus a Hg-HgO reference electrode.

Section 3

SYSTEMS DESIGN STUDIES

3.1 SMALL HYDRAZINE-OXYGEN FUEL CELL BATTERY

Some of the power-weight-time characteristics of small, lightweight fuel cell batteries are presented in Fig. 16. These tentative estimates, based on actual performance data, are considered to be conservative. Additional estimates for larger power units are continuing, based on the findings of the contracted investigations.

3.2 FUELS EVALUATION

In Table 8, for estimation purposes, is a list of theoretical weight requirements for a 280-watt, 35-day power source. These tentative calculations are based on the reversible potentials (Ref. 1) and an assumed coulombic efficiency of 100 percent. The results provide a basis for comparison of various systems. Cell EMF's for aqueous systems have been calculated for reversible reduction of oxygen to either perhydroxyl or hydroxyl ions. The last four entries in the table are for high-temperature systems operating at 150°C. Calculations are based on storage of all fuels and oxygen as liquids.
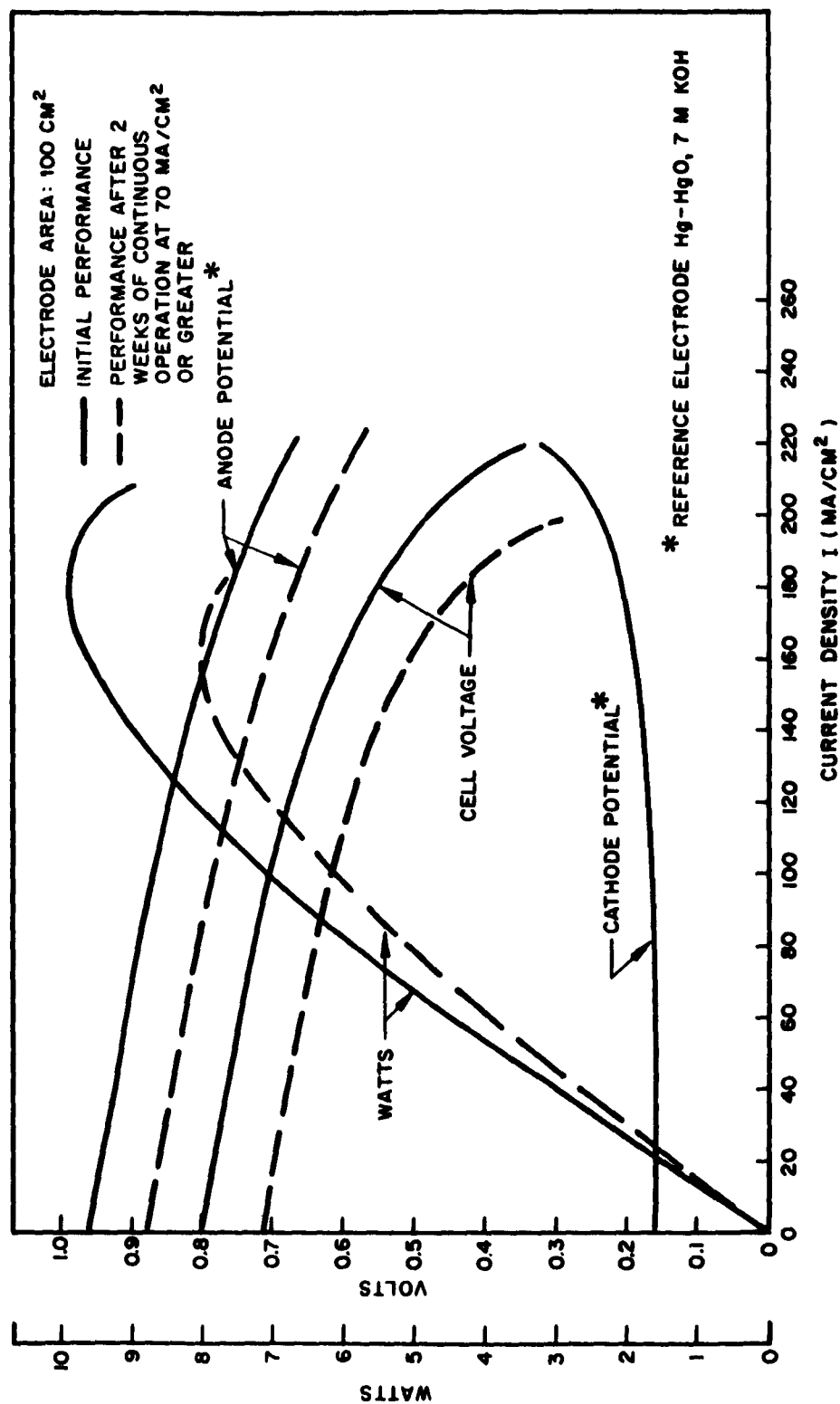
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Fig. 16 Projected Operational Characteristics for LMSC Hydrazine-Oxygen Fuel Cell Battery System

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Table 8

ENERGETICS OF SELECTED FUEL CELL SYSTEMS

Fuel	Oxidant With or Without Peroxide Mechanism	$E°$ (volts) 25°C	Fuel + Oxidant or Fuel Alone $\left(\frac{watt/hr}{lb}\right)$	Estimated Weight of Reactant Storage Containers (lb)	Weight of Fuel + Oxidant (lb)	Total Weight (lb)
				280 watts, 35 days		
NH_3 (g)	O_2	1.124	1,000	130	235	365
	(HO_2^-)	0.681	605		388	
NH_3 (g)	Air	1.124	2,410	9.5	97.5	107
	(HO_2^-)	0.681	1,459		161	
N_2H_4 (g)	O_2	1.56	1,185	96.2	198	294.2
	(HO_2^-)	1.12	805		292	
N_2H_4 (g)	Air	1.56	2,370	8.7	99.1	107.8
	(HO_2^-)	1.12	1,705		137.6	
H_2 (g)	O_2	1.23	1,661	223.5	141.5	365
	(HO_2^-)	0.787	1,065		221.0	
H_2 (g)	Air	1.23	14,950	102.3	15.7	118
	(HO_2^-)	0.787	9,570		24.6	
CH_3OH (g)	O_2	1.19	1,086	123	216	339
	(HO_2^-)	0.747	682		344	
CH_3OH (g)	Air	1.19	2,710	9	86.7	95.7
	(HO_2^-)	0.747	1,700		138.1	
CH_3OH (l)	O_2	1.185	1,080	123	218	341
	(HO_2^-)	0.742	675		348	
CH_3OH (g)	Air	1.185	2,700	9	87	96
	(HO_2^-)	0.742	1,685		139.5	
CH_3OH (g)	O_2	0.234	1,130	123	208	331
CH_3OH (g)	Air	1.234	2,820	9	80	89
C_4H_{10} (g)	O_2	1.12	1,335	129.6	176	305.6
C_4H_{10} (g)	Air	1.12	6,120	8.1	38.4	46.5

Section 4

FUTURE WORK

Work on Phase I will continue with respect to analysis of acid electrolyte systems and polarization components with possible applications of interrupter techniques. The cathode work will continue with nitrogen dioxide and oxygen or air systems. The feasibility of the acid-system fuel cell will be studied.

Work on Phase II will be initiated. In this phase, optimization of design parameters and studies of energy and material balances will be carried out. The heat-balance and heat-transfer problem will be considered from the standpoint of a general solution for application, using an analog computer.

A consultant will be retained for work on Phase II.

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Section 5
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Appendix A

PREPARATION OF BLACK PLATINUM, POROUS NICKEL ANODE

The black platinum, porous nickel anode was prepared by the following procedure:

- Degrease the porous nickel matrix.
- Etch the porous nickel plate for 3 min after the appearance of bubbles in a 15-percent HCl bath at room temperature.
- Wash in distilled water.
- Electroplate at 50 ma/cm^2 for 300 sec in a bath of 120 grams of chloro-platinic acetate (40 percent by weight platinum) and 1.2 grams of lead acetate, to which distilled water is added until the total volume is 1000 cc; use no agitation. (A platinum anode may be used during the plating.)
- Wash thoroughly in distilled water.
- Dry in a vacuum at 120°C for 2 hr.
- Fire in a hydrogen atmosphere at 300°C for 1 hr and cool in argon.